Electrokinetic deposition of individual carbon nanotube onto an electrode gap

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This paper presents a method for deposition an individual carbon nanotube (CNT). The alignment of a single CNT is very useful to perform studies related to applications in FET (Field Emitted Transistor), SET (Single Electron Transistor) and to make chemical sensor as well as bio sensors. In this study, we develo ped the deposition method of a CNT individualized in a solution. Using the electrokinetic method, we found the optimum conditions to assemble the nanotube and discussed about plausible explanation for the assembling mechanism. These results will be available to use for making the CNT sensor device.

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1. Introduction

Since discovered in 1991, carbon nanotube has been studied for many applications in science and engineering fields [1,2]. This material has attractive properties such as nano size, high aspect ratio, and large surface volume as geometrical characteristics. Moreover, CNT can be a semiconductor or a metal according to its chirality. Using CNT, many nano electronic devices such as memory, logic unit, and sensor have been investigated, because CNT has many superior properties than other materials [3,4,5]. However, many researchers have faced great difficulty to use the CNT in their device, because to align and assemble the CNT is very tricky. Especially individual CNT is invisible in optical microscope and it is uncontrollable in general manipulator because of its small size. Many methods to align the CNT have been developed. Growth method by CVD (Chemical Vapor Deposition) is very popular to align and assemble the CNT, but has problems in spacing control between the nanotubes, chirality control and high temperature growth condition [6,7]. Manual attachment using nano manipulator in SEM (scanning electron microscope) is an alternative method to handle the individual carbon nanotube, but there are several disadvantages such as time consuming work, expensive apparatus, and difficulty to handle the single walled carbon nanotube (SWNT) [8]. Chemical methods using self assembly monolayer (SAM) have been reported as well[9,10]. This method has advantages such as no need for expensive apparatus and short work time, while more researches to achieve small SAM patterns and repeatable chemical reaction should be conducted.

In this study, we report the electrokinetic method to assemble the nanotube on an electrode gap which was made by micro fabrication process with a wafer. This method is based on the dielectrophoresis (DEP) phenomenon which is aroused from polarization of the particle induced by the non-uniform electric field in a dielectric fluid [11]. DEP is a very simple and efficient method to assemble the nanotube, because it does not require expensive instrument, high temperature condition and chemical reaction. In the following section, we discuss about the theoretical background of assembling mechanism, analysis for electric field, experimental setup and results.

2. Theoretical background and Analysis

2.1 Theoretical background

Dielectrophoresis arises from the force imbalance exerted on the induced dipole moment of an uncharged dielectrics and/or conductive particle by a nonuniform electric field. The direction of this force depends on the total polarizability of the particle and the medium. As shown in Fig. 1, a particle is polarized in a medium, and moved to the electrode according to the positively or negatively charged condition [11,12,13]. During CNT assembly by electric field in a fluid medium, CNT experiences several kinds of forces such as viscous force, gravity, Brownian motion, and DEP force. Among these forces, DEP force is large enough to dominate the movement more than the other forces. So we focused only on the DEP force. In the CNT assembly experiment, we used a dielectric solution (Ethanol or Dichloroethylene) to disperse the CNT.

Dielectrophoretic force can be written as

$$F_{DEP} = \frac{1}{2}\pi r^2 l \varepsilon_m \,\mathrm{Re}(K_L)\nabla|E|^2 \tag{1}$$

$$K_L = \frac{\varepsilon_p^* - \varepsilon_m^*}{3\varepsilon_m^*}$$

where the Clausius-Mossotti factor, K_L, is related to the complex dielectric constant of the particle (ε_p) and the medium (ε_m).

$$\varepsilon_m^* = \varepsilon_m - j\frac{\sigma_m}{\omega} \tag{2}$$

$$\varepsilon_p^* = \varepsilon_p - j\frac{\sigma_p}{\omega} \tag{3}$$

where j is a complex number, σ is the conductivity and ω is the applied frequency.

As shown in the Eq.(1), DEP force can be either the positive or negative in terms of the Re(K_L) factor which is dependent on ε,σ,and ω. In this case, particle represents the CNT and the medium represents the Ethanol (multi walled carbon nanotube, MWNT) or Dichloroethylene (SWNT). The logarithmic plot of real parts of the Clausius-Mossotti factor, K_L, using constants of Table 1 (Fig. 2), shows that MWNT is positive over most of the frequency range. SWNT would have metallic and semiconducting property. In this case, Re(K_L) of semiconducting SWNT is too small so they do not affect our system. However, Re(K_L) of metallic SWNT is always positive and they affect our system. Therefore, if we use a particular frequency, we expect to have a positive DEP system.

In general, controllable factors to assemble the CNT are theoretically frequency, material properties of the medium, applied voltage and geometry of the electrode. The geometry of the electrode can affect the gradient of the electric field. It was known that CNT would be aligned along with the direction of the electric field line. Frequency of the applied voltage also affects the magnitude of the DEP force, because the complex permittivity spectra of the CNT and ethanol are the function of the frequency. When we apply the electric field, the polarized CNT affects the DEP force, and is attracted to the highest gradient of the electric field. In this situation, the longer nanotube experiences larger force than the small size particles such as impurities. However, if there are larger impurities than the nanotube, impurities would arrive at the highest electric field gradient. In this case, we have a symmetric geometry in the view of the electric field distribution as shown in Fig. 1. If we apply a high frequency of over 1 MHz, the CNTs have no response to the polarity of the electrode, because the change of the polarity is too fast. So the CNTs may move to either side of the electrodes. Consequently, the CNTs would tend to move to the closer electrode.

2.2 Analysis

We analyzed the geometrical effect on the electric field distribution. As for the top point of the electrode, the sharp edge and the round edge are compared. Both types have a 4 μm gap between the electrodes as shown in Fig. 3. Surface distribution of the nominal electric fields are shown in Fig. 3. The maximum electric fields are 1.63 V/μm and 3.67 V/μm for round and sharp edge electrode, respectively. In the case of the sharp electrode, the electric field is concentrated on the sharp edge. Therefore, it would be difficult to find the place to hold the CNT. When the CNT is attracted to this region, the moving speed becomes maximum at the edge point so that the CNTs would be apt to pass by the sharp edge. However, in the case of the round shape of the electrode, electric field gradient changes smoothly near the round edge. This means that the moving speed of the CNT slows down near the round edge. In Eq. (1), we can find the locations of $\nabla E^2 \approx 0$ at the middle area of the round edge, indicating that there is little DEP force. Therefore the round shape would be more preferable to assemble the nanotube compared with the sharp shape, because we could get a wider stable area to hold the CNT.

As for the parallel shaped electrode, in the top view, the electric field distribution between the electrodes must be orthogonal to the electrode side as shown in Fig. 4(a). Particles experience a DEP force only when the electric field is nonuniform. However, we could not expect a non-uniform electric field in this area. But the experimental results show that the CNTs were assembled in this type of electrode[13]. This is due to misleading 2-dimensional approach to explain the DEP phenomenon. In Fig. 4(b), we presented the side view of the electrode. Considering the above results, even if we make the electrode parallel shaped, the CNTs would be attracted to the gap of the electrode, because the non-uniform electric field over this gap exists in the vertical direction as shown in Fig. 4(b).

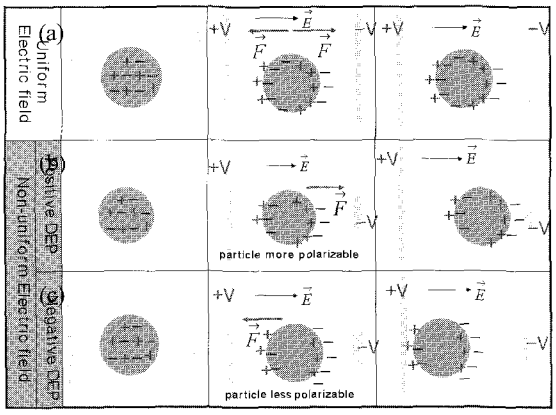

Fig. 1 (a) In uniform electric field, a particle does not move to any direction because induced forces are completely balanced. In contrast in a non-uniform electric field, (b) High polarized particle which has totally positive charge moves to the high electric field (-V): Positive DEP, (c) Less polarized particle which has the totally negative charge moves to the positive electric field(+V): Negative DEP

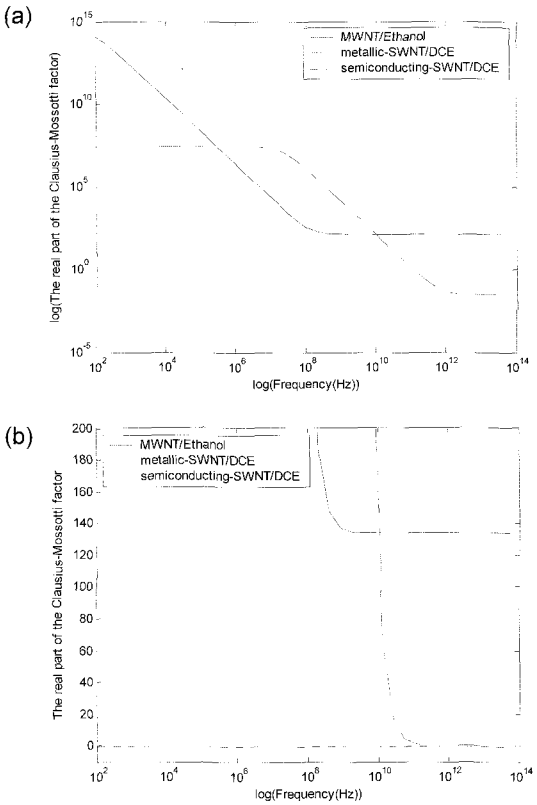

Fig. 2 (a) The logarithmic plot of real parts of the Clausius-Mossotti factor, K_L, for metallic MWNT particle in ethanol medium, and for metallic and semiconducting SWNT particle in Dichloroethylene medium. (b) Magnified plot of real parts in high frequency region

Based on the theoretical background and analysis result, the possibility of assembling a single bridged CNT on an electrode gap may be investigated. In this study, the experimental parameters are the solution density and the magnitude of the applied voltage, which actually controls the DEP force. Therefore, after the first CNT is placed on to the electrode gap, if the solution dries out before the arrival of the second CNT at the gap, we are able to make the single deposition of the CNT. It requires very precise tuning of the experimental conditions.

Table 1 Electrical properties of carbon nanotube and medium

		Conductivity (S/m)	Permittivity (F/m)
Particle	Metallic MWNCT	1e8	8.854e-8
	Semicond-ucting WCNT	1e-3	8.854e-12
	Metallic SWCNT	1e-7	100e-12
Medium	Ethanol	0.13e-6	220e-12
	Dichloroethylene	1.24e-2	91.7e-12

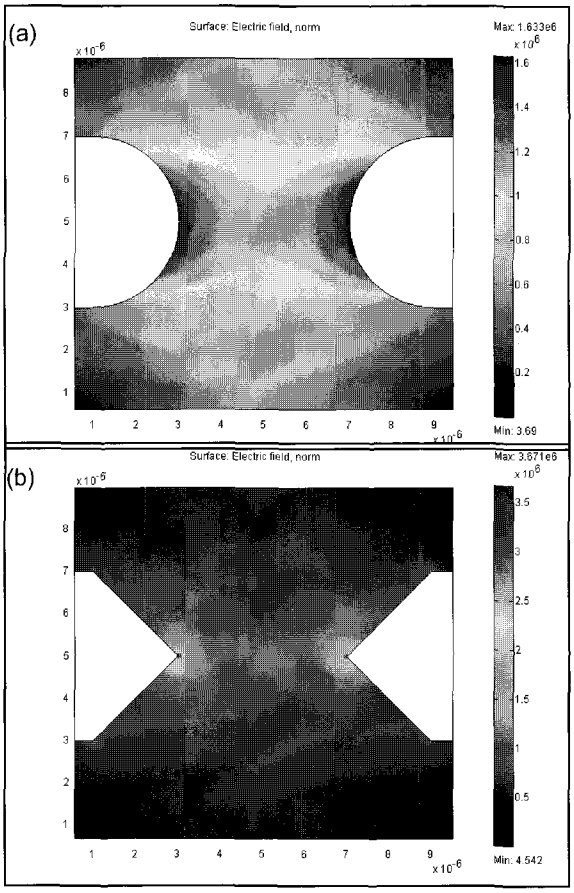

Fig. 3 Simulation result of (a) round electrode and (b) sharp electrode in the case of 5 Vrms. These results show the contour surface of the nominal electric field using commercial FE(finite element) software, FEMLAB

3. Experimental setup

For this experiment, we fabricated the electrode as shown in Fig. 5 using micro lithography. On a silicone wafer, 200nm SiO_2 was deposited to insulate between the metal electrode and the wafer. This structure could be used for making the source-drain structure with the bottom gate. As the next step, a 50 nm aluminum layer was also deposited onto the SiO_2 layer to serve as the electric conductor shown in Fig. 5(a). We used an electrode array with 10 gaps, because we could check the availability and the possibility of the single-bridged CNT deposition at once. In microscopic view, these results are similar to 10 individual experiments for one electrode gap (Fig. 3(b)). We fabricated two kinds of gap distance, 2 μm for MWNT and 4 μm for SWNT.

Experimental setup is presented in Fig. 6. This setup is very simple and need only a function generator. In order to verify the input signal before the experiment, we could check the applied signal using an oscilloscope. In this experiment, first we made a CNT solution which was dispersed with Ethanol or Dichloroethylene. To check the density, we measured the CNT quantity exactly using a mass balance. The CNT solution was sonicated for a few minutes to be uniformly dispersed. Next, we dropped a 1 $\mu\ell$ solution with a pipette on the gap array, and then waited for a few minutes until the solution was dried out. MWNT which was made by arc discharge was used for this experiment. This CNT solution had many impurities so that it was not easy to assemble the individual CNT. Therefore, MWNTs used in this experiment were purified by acid treatment and centrifuge. Sample dropped on a wafer piece is shown in Fig. 7(a).

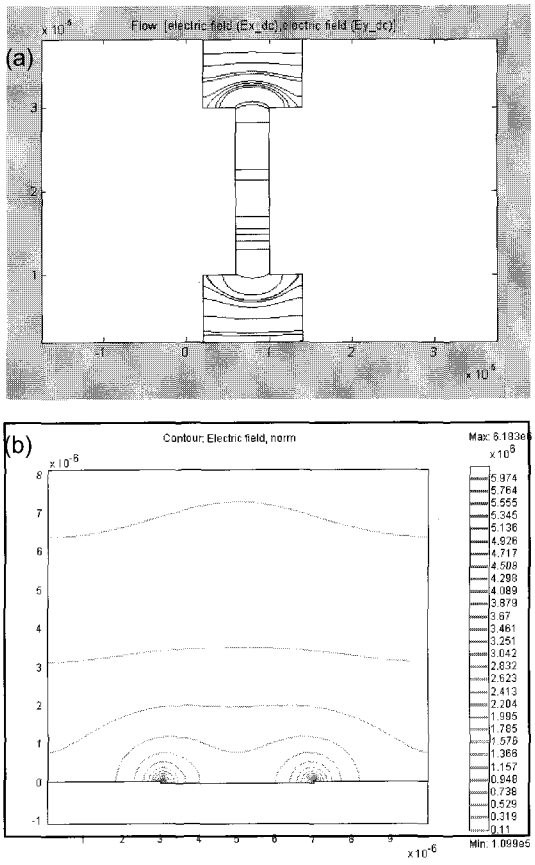

Fig. 4 Simulation result for (a) the top view of the parallel electrode and (b) the side view in the case of 5 Vrms. These results show that a non-uniform field over the upper area of the electrode has formed

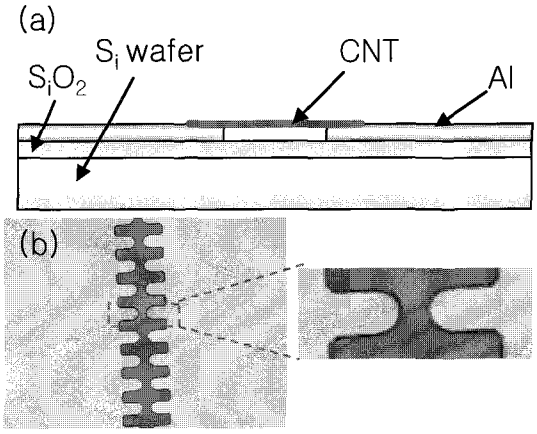

Fig. 5 (a) Schematic view of the micro fabrication process of the electrode. The CNT is assembled by a separate attaching process. (b) The fabricated electrode array with 10 electrodes. The electrode gap distance is 2.5 μm or 4 μm

If the impurity particle is smaller than the CNT, it would have little effect on the CNT assembly process. SWNT sample made by laser ablation had high purity and the average length was 5~10 μm (Fig. 7(b)). It was ideal for assembling the nanotube using dielectrophoresis.

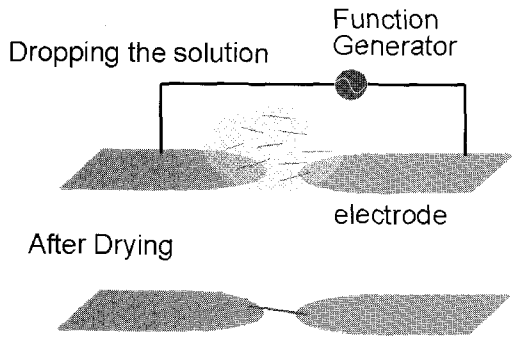

Fig. 6 Schematic of the experiment for CNT assembly across the electrode gap

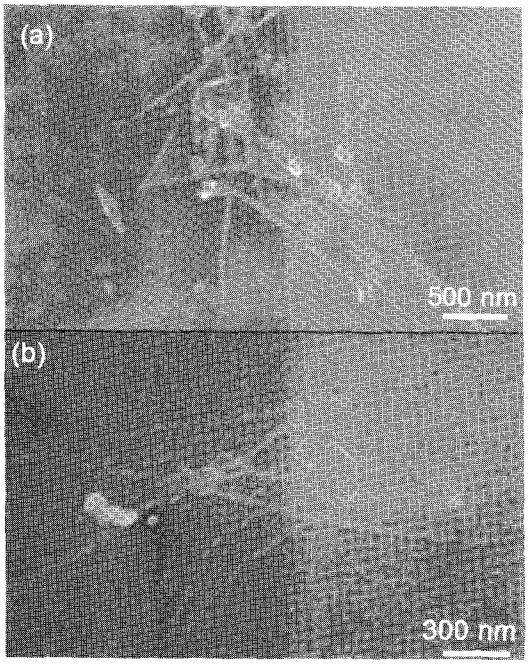

Fig. 7 SEM image of (a) the purified MWNT. Round shaped impurities are shorter than CNT. The CNT average length is 2~3 ㎛. This shortened nanotube is due to the acid treatment and sonication during a long time. (b) The bundle of SWNT untangled by chemical treatment and centrifuge. There are little of the impurities

In the natural state in a solution, the nanotube would be bundled and tangled. Therefore, sonication process is necessary to separate the nanotube before the experiment.

4. Result and Discussion

Firstly, in order to verify the effect of the density of the MWNT solution, we changed the solution density as 1 ㎍/㎖, 5 ㎍/㎖, and 10 ㎍/㎖. In the case of 1 ㎍/㎖, we could not find the assembled nanotube at the electrode gap. 5 ㎍/㎖ might be an adequate density to assemble the individual nanotube (Fig. 8(a)). In the case of 10 ㎍/㎖, too many nanotubes were deposited onto the electrode gap (Fig. 8(b)). The above experiments were conducted at 10 volts at 5MHz.

Next, we changed the applied voltage under the conditions of 5 ㎍/㎖ and 5 MHz. As shown in Fig. 9(a), 10 volts is an adequate condition to assemble the single MWNT. When we applied the electrical input at 25 volts, many nanotubes were deposited on the electrode gap as shown in Fig. 9(b). In this case, the assembling time was about 30 seconds. Among the electrode gaps in an array, single MWNT has been assembled at 3 electrode gaps (30% yield). Under the 10 volts, we could not find any deposition of an individual MWNT.

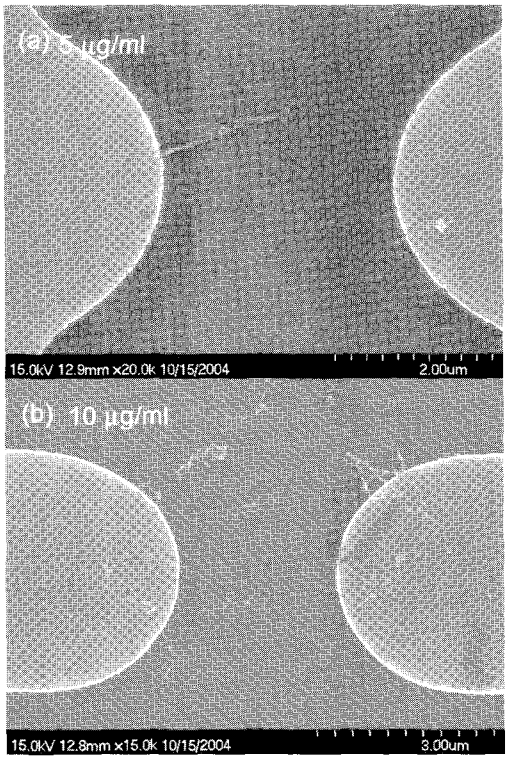

Fig. 8 The experimental results for density change (a) 5 ㎍/㎖ (b) 10 ㎍/㎖ at 10V input and 5 MHz frequency

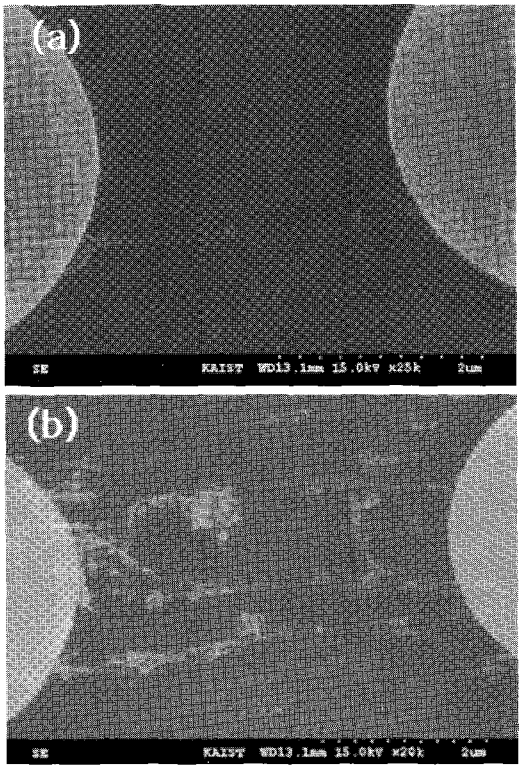

Fig. 9 Assembled results at (a) 10Volt and (b) 25Volt at 5 MHz in the case of 5 ㎍/㎖

These experiments depend on the sample condition. So if we change the test sample, the assembling condition would also be slightly changed. In some cases, when MWNTs were shortened less than the gap distance of 2 ㎛, a MWNT firstly attached at the edge of the electrode, and the other MWNT was connected to the previously attached MWNT like a chain so that it would make a full bridge across the electrode pair.

As for a SWNT, we changed only the magnitude of the applied voltage. When we applied 5 volts, 5~6 gaps among the 10 gaps were assembled into one or two bundles of SWNTs (Fig. 10(a)). When we increased the applied voltage, many CNTs were deposited across the gap (Fig. 10(b)). In the case of below 5 volts, we could not find the deposition of single bundle of SWNTs, even though there were protruded nanotubes but not connected ones across the gap.

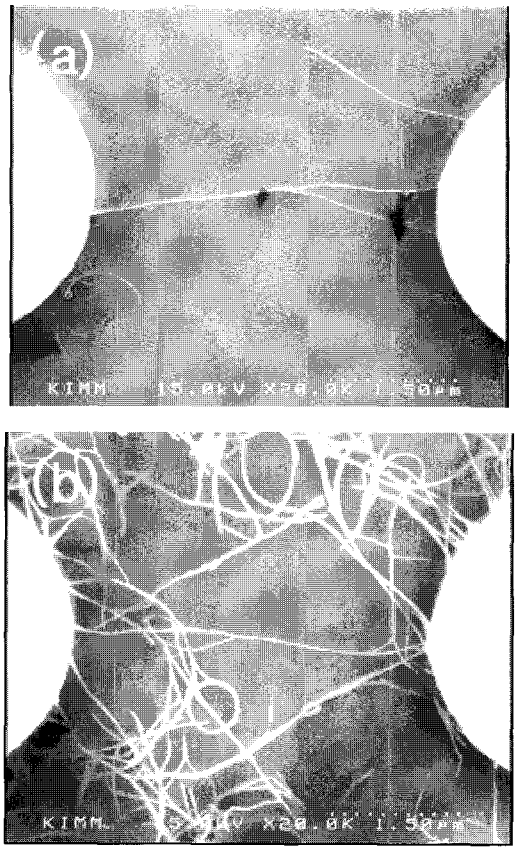

Fig. 10 Results for SWNT in the cases of (a) 5 Volt (b) 10 Volt at 5MHz and 1 $\mu g/m\ell$

5. Conclusions

In this study the deposition characteristics of individual CNTs onto an electrode gap was investigated. Electrokinetic mechanism was utilized as the major driving force for the deposition process.

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